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(54) **CYCLIC CATALYST REGENERATION
PROCESS USING ADSORPTION AND
DESORPTION ON VENT STREAM**

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(58) **Field of Search** 502/35, 50, 52,
502/53; 208/140

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,336,834 A	8/1994	Zarchy et al.	585/737
5,965,473 A	10/1999	Sechrist et al.	502/35
6,117,809 A	9/2000	Sechrist et al.	502/35

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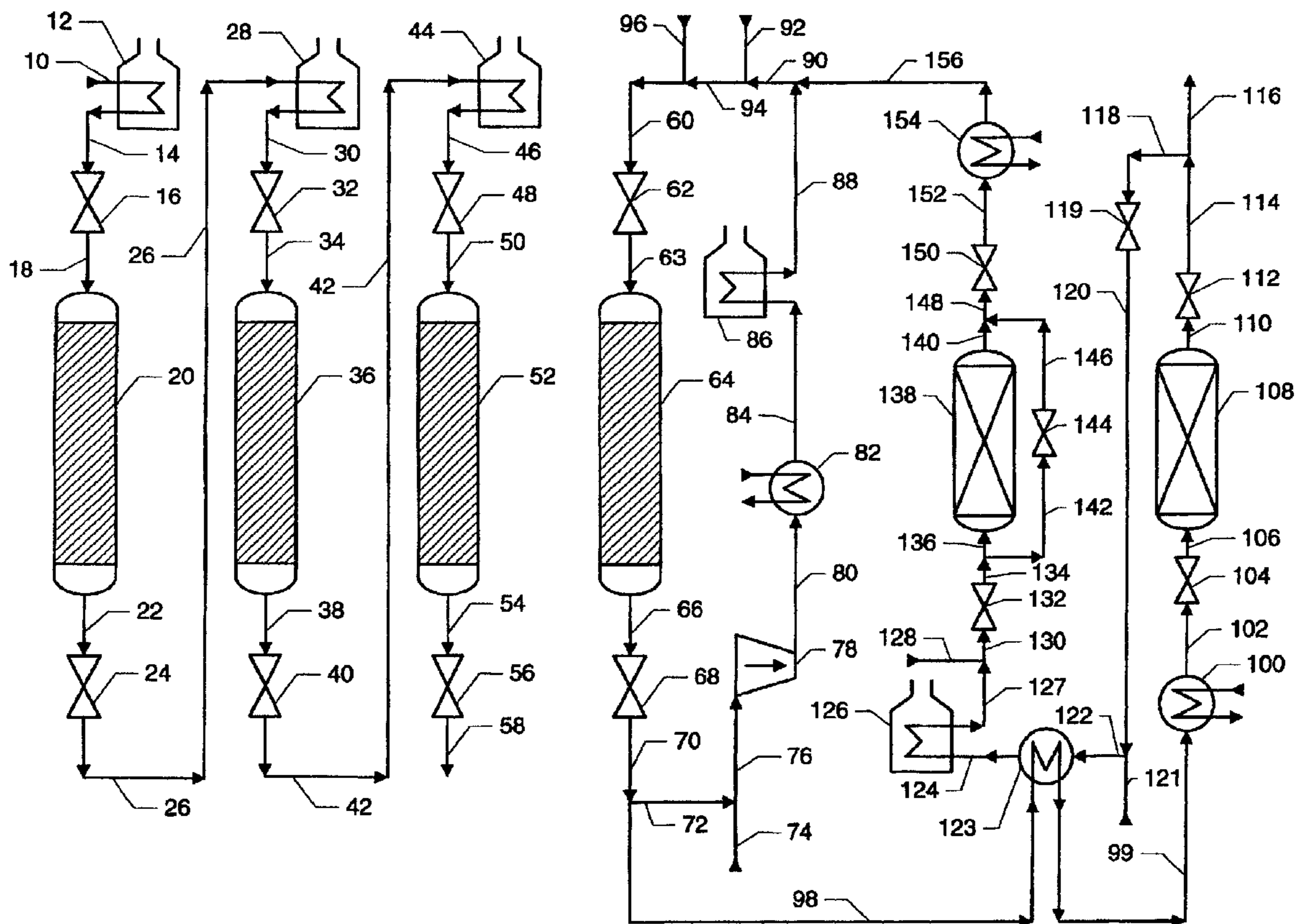
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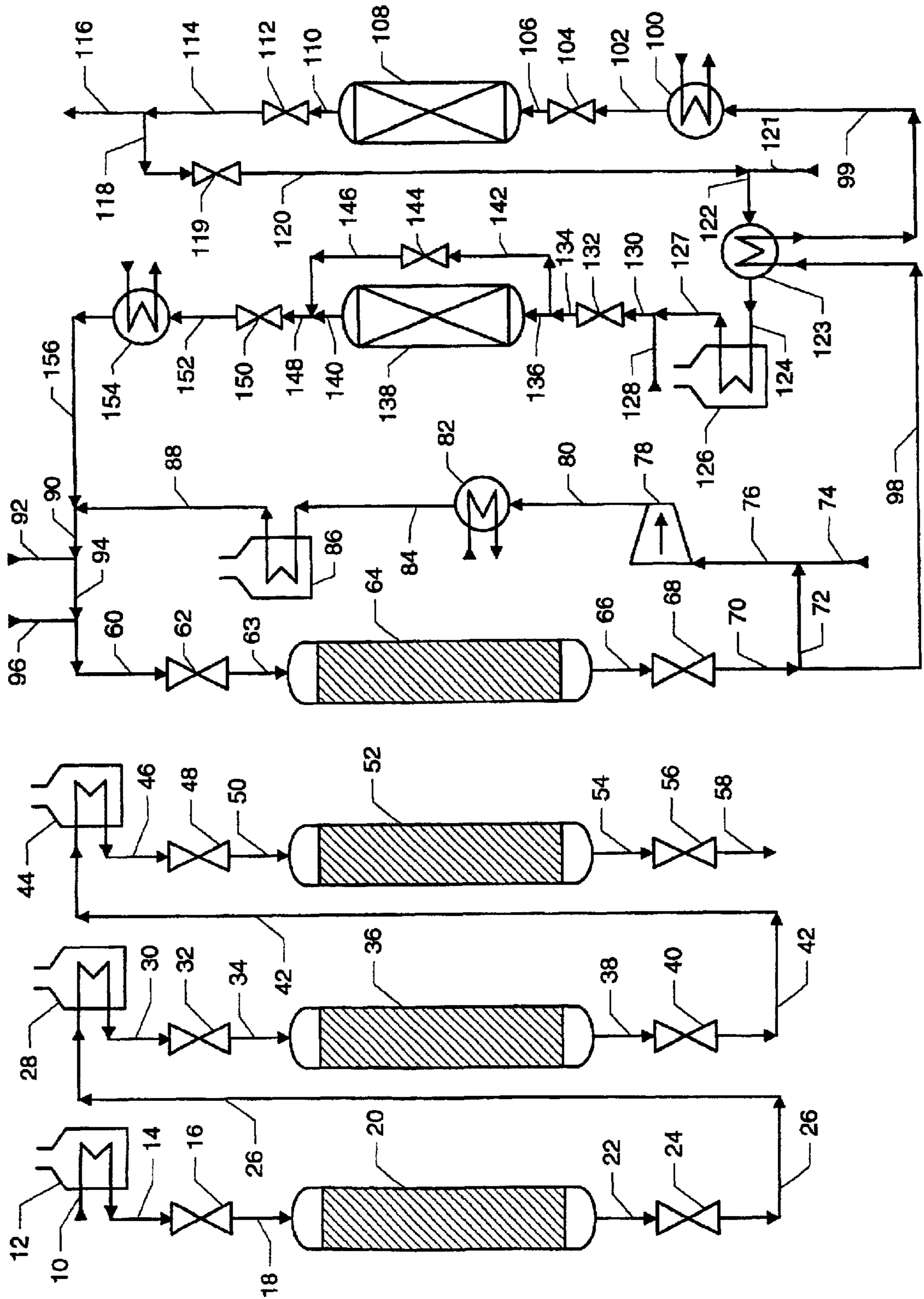
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(57) **ABSTRACT**

A method of recovering halogen-containing materials from the cyclic catalyst regeneration operation of a catalytic hydrocarbon conversion process is disclosed. The method uses an arrangement of beds of adsorbent to return the halogen-containing materials to a circulating regeneration circuit.

22 Claims, 1 Drawing Sheet





**CYCLIC CATALYST REGENERATION
PROCESS USING ADSORPTION AND
DESORPTION ON VENT STREAM**

FIELD OF THE INVENTION

This invention relates generally to the regeneration of hydrocarbon conversion catalysts in the presence of a halogen-containing material.

BACKGROUND OF THE INVENTION

Numerous hydrocarbon conversion processes are widely used to alter the structure or properties of hydrocarbon streams. Such processes include isomerization from straight chain paraffinic or olefinic hydrocarbons to more highly branched hydrocarbons, dehydrogenation for producing olefinic or aromatic compounds, reforming to produce aromatics and motor fuels, alkylation to produce commodity chemicals and motor fuels, transalkylation, and others.

Many such processes use catalysts to promote hydrocarbon conversion reactions. These catalysts tend to deactivate for a variety of reasons, including the deposition of carbonaceous material or coke upon the catalyst, sintering or agglomeration or poisoning of catalytic metals on the catalyst, and/or loss of catalytic metal promoters such as halogens. Consequently, these catalysts are typically reactivated in a process called regeneration. Reactivation can thus include, for example, removing coke from the catalyst by burning, redispersing catalytic metals such as platinum on the catalyst, oxidizing such catalytic metals, reducing such catalytic metals, replenishing catalytic promoters such as chloride on the catalyst, and drying the catalyst.

One of the problems during regeneration of halogen-containing catalysts is loss of halogen itself from the catalyst. This happens when the catalysts are contacted with gases that, while regenerating the catalyst, tend also to remove halogen from the catalyst.

U.S. Pat. No. 5,965,473 discloses a method for recovering chlorine-containing materials from the effluent gases during catalyst regeneration in a hydrocarbon conversion process with a cyclic regeneration operation. To prevent loss of chlorine-containing materials, U.S. Pat. No. 5,965,473 uses one of the off-stream catalyst beds. This is an inefficient use of the vessel that contains the off-stream catalyst bed as well as of the catalyst itself, both of which could be better used for promoting hydrocarbon conversion reactions. Therefore, more efficient methods are sought to decrease the loss of halogen during halogen-containing catalyst regeneration.

SUMMARY OF THE INVENTION

This invention is a catalyst regeneration process that uses a bed of adsorbent zone first to adsorb halogen-containing materials that are removed from catalyst undergoing regeneration, and then to desorb these halogen-containing materials so they are re-adsorbed on to catalyst that is undergoing regeneration. The bed of adsorbent, therefore, is contacted with streams and/or at conditions that are different from those used during hydrocarbon conversion. This invention does not use a reaction vessel and its catalyst to adsorb and desorb the halogen-containing materials.

One object of this invention is to improve processes for regeneration of hydrocarbon conversion halogen-containing catalysts. Another object is to recover halogen-containing materials that are present during catalyst regeneration. A third object is to improve the utilization of equipment and

catalysts used in hydrocarbon conversion processes, including reforming, isomerization, and dehydrogenation. A fourth object is to improve the efficiency of cyclic catalyst regeneration processes.

5 In a broad embodiment, this invention is a process for the regeneration of a hydrocarbon conversion catalyst in the presence of a halogen-containing material. The process comprises contacting a regeneration inlet stream comprising a first component selected from the group consisting of oxygen, hydrogen, nitrogen, and a C₁-C₅ hydrocarbon with a catalyst in the presence of a halogen-containing material at regeneration conditions to at least partially regenerate the catalyst and produce a regeneration effluent stream comprising the material and the first component; contacting a first portion of the regeneration effluent stream with an adsorbent, adsorbing the material on the adsorbent at adsorption conditions, and recovering an adsorption effluent stream comprising the first component and having a reduced concentration of the material relative to the first portion of the regeneration effluent stream; contacting a desorption inlet stream comprising a second component selected from the group consisting of oxygen, hydrogen, nitrogen, and a C₁-C₅ hydrocarbon with the adsorbent, the adsorbent having the material adsorbed thereon, desorbing the material from the adsorbent at desorption conditions, and recovering a desorption effluent stream comprising the material and the second component; and, forming the regeneration inlet stream from a second portion of the regeneration effluent stream and at least a portion of the desorption effluent stream.

Other embodiments and objects are described in the detailed description of the invention.

Information Disclosure

35 U.S. Pat. No. 5,336,834 (Zarchy et al.) discloses an adsorption zone in combination with a catalytic hydrocarbon conversion process that keeps chlorine-containing compounds in the catalyst bed and prevents contamination of product streams with chlorine-containing compounds. The contents of U.S. Pat. No. 5,336,834 are hereby incorporated herein by reference.

45 U.S. Pat. No. 5,965,473 (Sechrist et al.) discloses a method for recovering chlorine-containing materials from the effluent gases during catalyst regeneration in a hydrocarbon conversion process with a cyclic regeneration operation. The contents of U.S. Pat. No. 5,965,473 are hereby incorporated herein by reference.

50 U.S. Pat. No. 6,117,809 (Sechrist et al.) discloses a method for recovering chlorine-containing materials removed from a chloride-containing catalyst undergoing reduction by using a sorption zone which contains catalyst. The contents of U.S. Pat. No. 6,117,809 are hereby incorporated herein by reference.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a process flow diagram showing an embodiment of the invention.

DETAILED DESCRIPTION OF THE
INVENTION

65 This invention recovers halogen-containing materials especially chlorine-containing materials removed from hydrocarbon conversion catalysts undergoing cyclic catalyst regeneration. These materials, which are present in a portion of the regeneration effluent which is vented from the

process, are absorbed from that portion on an adsorbent contained in at least one adsorption bed. Once the adsorption bed has adsorbed the halogen-containing material, the halogen-containing materials are desorbed from the bed. Desorption takes place using a stream that is introduced to the process to regenerate the catalyst. When this introduced stream combines with a recycled portion of the regeneration effluent and the combined stream contacts catalyst that is undergoing regeneration, the halogen-containing materials are returned to the catalyst.

This invention uses at least one adsorbent. The adsorbent reversibly adsorbs at least one halogen-containing material. Suitable adsorbents include molecular sieves such as zeolites, clays, inorganic polymers such as alumina and activated alumina, zirconia, carbon, activated carbon, organic polymers such as resin adsorbent, etc. Suitable aluminas include gamma, alpha, theta, etc. Suitable adsorbents also include the ion exchanged clinoptilolites described in U.S. Pat. No. 5,336,834. Preferably, the adsorbent is selected so that the conditions at which the adsorbent has a capacity for reversible adsorption correspond to the conditions for cyclic regeneration. In addition, the adsorbent's select physical properties that affect reversible adsorption preferably do not degrade significantly when the adsorbent is used for adsorption and desorption. For example, while adsorbents with high surface areas are preferred, it is also preferred that the repeated use of the adsorbent for adsorption and desorption does not significantly decrease the adsorbent's surface area. Thus, while silica gel may be used as the adsorbent, it is not preferred. Although the adsorbent may contain an IUPAC Group 8-10 (VIII A) or noble metal component such as gold, silver, platinum, palladium, iridium, rhodium, mercury, ruthenium, or osmium, the adsorbent contains preferably less than 0.1 wt-%, and more preferably none, of the metal, based on the weight of the adsorbent. More than one adsorbent may be used. Multiple adsorbents may be combined into a composite material, or they may be used without compositing, such as in a physical admixture of two adsorbents.

In addition to reversibly adsorbing at least one halogen-containing material, the adsorbent may also reversibly adsorb water. Generally, water is present along with the halogen-containing material in the cyclic regeneration stream from which the halogen-containing material is recovered. Generally, the conditions that result in reversible adsorption of the halogen-containing material also result in reversible adsorption of water. However, the presence of water can affect, sometimes adversely, the adsorption of the halogen-containing material, because water can compete with the halogen-containing material for sites on the adsorbent.

This invention is believed to be applicable to a wide range of catalytic hydrocarbon conversion processes and the regeneration of their catalysts, including aromatic isomerization, paraffin or olefin isomerization, paraffin dehydrogenation, and alkylation. However, catalytic reforming is the most widely practiced hydrocarbon conversion process which uses cyclic catalyst regeneration and to which this invention applies. Reforming catalysts typically contain a halogen, such as chlorine. Catalytic reforming is described in U.S. Pat. No. 5,965,473, the contents of which are hereby incorporated herein by reference.

This invention is applicable to many of the individual regeneration steps that typically comprise a cyclic regeneration operation of a catalytic reforming process. These include coke combustion, redispersion of catalytic metal on the catalyst, rehalogenating of the catalyst, drying of the

catalyst, and reduction of catalytic metal on the catalyst. Except for drying, these steps are described in U.S. Pat. No. 5,965,473. Drying can occur by contacting the catalyst with a gas containing oxygen, hydrogen, nitrogen, or a C₁-C₅ hydrocarbon, or a mixture thereof, under conditions such that water is transferred from the catalyst to the gas. Preferably the gas does not react with the catalyst, any component thereof, or any deposit thereon. Drying conditions usually comprise an elevated temperature and/or a reduced pressure and/or an elevated gas hourly space velocity, including the temperatures, pressures, and gas hourly space velocity described for the other regeneration steps in U.S. Pat. No. 5,965,473. Usually the water-containing effluent from the drying step is itself dried and then recycled to the catalyst bed to further dry the catalyst. Drying of the effluent usually takes place first by cooling the gas and then condensing the water and/or by contacting the gas with a desiccant. When drying involves cooling the gas, the gas is normally reheated prior to recycling.

The drawing shows a cyclic reforming process using three on-stream reactors **20**, **36**, and **52**, and a fourth off-stream reactor **64** which is undergoing regeneration. Only the equipment and lines necessary for an understanding of the invention are shown in the drawing. The reactors have inlet lines **18**, **34**, **50**, and **63** containing valves **16**, **32**, **48**, and **62**, which can be opened or closed to start or stop flow to each reactor. They also have outlet lines **22**, **38**, **54**, and **66** containing valves **24**, **40**, **56**, and **68**, which can be opened or closed to start or stop flow from each reactor. Well-known equipment and lines (not shown) connect the reactors to each other so that each on-stream reactor can be taken off-stream and regenerated in the place of off-stream reactor **64**, and so that the off-stream reactor **64** can be placed on-stream and function as any of the on-stream reactors. Although this description is mainly in terms of three on-stream reactors and one off-stream reactor, there may of course be more or fewer on-stream reactors or off-stream reactors, and some off-stream reactors may have already undergone regeneration, while others may be awaiting regeneration.

A combined feed stream comprising naphtha and hydrogen flows through line **10**, is heated in heater **12**, passes through line **14**, valve **16**, and line **18**, and enters reactor **20**, where reforming reactions occur. Reactor **20** effluent flows through line **22**, valve **24**, and line **26**. Since reforming reactions are generally endothermic the effluent is heated in heater **28**, and the heated effluent flows through line **30**, valve **32**, and line **34**, and into reactor **36**. Effluent from reactor **36** flows through line **38**, valve **40**, and line **42**, is heated in heater **44**, flows through lines **46**, valve **48**, and line **50**, and enters reactor **52**. Reactor **52** effluent flows through line **54**, valve **56**, and line **58** to conventional product separation and recovery facilities (not shown).

The catalyst in off-stream reactor **64** is undergoing regeneration using a recirculating regeneration system that uses two beds **108** and **138** containing adsorbent such as alumina. Adsorbent bed **108** operates in adsorption mode and adsorbent bed **138** operates in desorption mode. Adsorption bed **108** has inlet line **106** containing valve **104**, which can be opened or closed to start or stop flow to the bed. Adsorption bed **108** also has outlet line **110** containing valve **112**, which can be opened or closed to start or stop flow from the bed. Desorption bed **138** has an inlet line **136**, another inlet line **134** upstream which contains inlet valve **132**, an outlet line **140**, and another outlet line **148** downstream which contains valve **150**. Desorption bed **138** also has bypass lines **142** and **146** and bypass valve **144**, which can be opened or closed to

start or stop bypass flow around desorption bed **138**. Well-known equipment and lines (not shown) connect the beds to each other so that the bed **108** in adsorption mode can be placed in desorption mode, and so that bed **138** in desorption mode can be placed in adsorption mode.

The following description is mainly in terms of the regeneration step being coke combustion, but this is not intended to limit the scope of this invention as set forth in the claims. Regenerant gas (also referred to herein as combustion gas) comprising oxygen, nitrogen, and a halogen-containing material (hydrogen chloride or chlorine) flows at an elevated temperature through line **60**, valve **62**, and line **63**, and enters reactor **64**. Since the combustion of coke deposits on the catalyst in reactor **64** is generally exothermic, the reactor **64** effluent gas (also referred to herein as flue gas) is hotter than the combustion gas. More importantly for this invention, the flue gas contains one or more halogen-containing materials that have been removed from the catalyst by the coke combustion, usually because of the combined effect of gas contacting, heat release, and any water produced. The flue gas flows through line **66**, valve **68**, and line **70**.

Since the flue gas stream contains carbon dioxide byproduct from coke combustion, a minor portion of these vapors is withdrawn from the recirculating gases through line **98**. The remaining (major) portion of these vapors recirculates by flowing through line **72**, where it combines with an oxygen-containing make-up stream (usually air) in line **74**. Preferably, the flue gas portions flowing in lines **98** and **72** are each aliquot portions of the flue gas stream flowing in line **70**. An aliquot portion of a stream is a portion of the stream that has substantially the same composition as the stream. Line **76** carries this gas stream to compressor **78**, which discharges into line **80**. Depending on how much heat from coke combustion and compression is carried by the gas stream flowing in line **80**, that stream may be cooled in exchanger **82**, heated in heater **86**, or both. Because the major portion of the flue gas is recycled to the inlet of off-stream reactor **64** using compressor **78**, whether or not exchanger **82** or heater **86** or both are needed depends mainly on the outlet and inlet temperatures of off-stream reactor **64**. Exchanger **82** can cool the flue gas flowing in line **80** by indirect heat transfer using water or air as a cooling medium. The gas stream from exchanger **82** flows through line **84**. Exchanger **82** is usually operated so that the temperature of the stream flowing in line **84** is such that, when the gas stream in line **84** is mixed with other gas streams described below to form the combustion gas stream flowing in line **63**, the combustion gas stream is at the desired regeneration temperature for the inlet of off-stream reactor **64**. If, however, the gas stream flowing in line **84** is relatively cool and as a result the inlet temperature for off-stream reactor **64** is less than the desired temperature, heater **86** may be used to heat the gases flowing in line **84** to attain the desired regeneration inlet temperature.

After any heating, the gases flow through line **88** and combine with a desorption effluent stream flowing in line **156** to form a stream that flows through line **90**. The stream in line **90** combines with a make-up stream (if any) in line **92**. The make-up stream can be used to add additional halogen to the stream flowing in line **90** to produce the gas stream flowing in line **94**. Averaged over time, the amount of halogen added through line **92** is approximately equal to the amount of halogen vented from the process with the adsorption effluent flowing in line **116**. But at any particular point in time, the amount of halogen added through line **92** is usually what is needed to attain the desired molar ratio of

water to halogen at the inlet of the off-stream reactor **64** for regeneration purposes.

The gas flowing in line **94** combines with another make-up stream (if any) in line **96**. The make-up stream in line **96** can be used to add additional water (or a compound that forms water after being added, such as an alcohol) to the stream flowing in line **94** to produce the combustion gas (regeneration gas) flowing in line **60**. The amount of water (or compound that forms water) added through line **96** is usually what is needed to attain the desired molar ratio of water to halogen at the inlet of the off-stream reactor **64** for regeneration purposes.

The portion of the flue gas that flows through line **98** contains halogen-containing material to be recovered in adsorption bed **108**. The flue gas enters heat exchanger **123**, which cools the flue gas stream by indirect heat exchange with the stream flowing in line **122** enroute to desorption bed **138**. The cooled flue gas flows through line **99** to cooler **100**, which further cools the flue gas using water or air as a cooling medium. The flue gas stream then flows through line **102**, valve **104**, and line **106**, and enters bed **108**, which contains adsorbent. Adsorbent bed **108** is operating in adsorption mode, and the adsorbent adsorbs at least some of the halogen-containing material from the cooled flue gas. The adsorption effluent flows through line **110**, valve **112**, and line **114**, and can be vented from the process through line **116**. If desired, this vented stream can be sent to conventional facilities (not shown) to neutralize any residual halogen that may be present in the stream. However, one of the advantages of this invention is that the residual halogen content of the adsorption effluent is so relatively low that the need for such an additional neutralization step is often eliminated.

Prior to being placed in adsorption mode, the bed of adsorbent **108** had operated in desorption mode in the position of bed of adsorbent **138**. While the bed **108** was in desorption mode, the halogen-containing materials on the adsorbent were desorbed and passed to the off-stream reactor (e.g., reactor **64**) that was undergoing regeneration at the time. This desorption depleted the adsorbent in bed **108** of halogen-containing materials, and thereby prepared the adsorbent in bed **108** for use in adsorption mode. Conversely, prior to being placed in desorption mode the bed **138** had operated in adsorption mode in the position of bed **108**. While the bed **138** was in adsorption mode, the halogen-containing materials from the off-stream reactor that was undergoing regeneration at the time were adsorbed on the adsorbent. This adsorption added halogen-containing materials to the adsorbent in bed **138**, and thereby prepared the adsorbent in bed **138** for use in desorption mode.

Gas for desorbing halogen-containing materials from bed **138** can be any suitable gas stream. In the case of the regeneration step being coke combustion or metal oxidation, the desorption inlet gas may be, for example, an oxygen-containing gas such as air or a diluent gas such as nitrogen. In the case of drying, the desorption inlet gas may be a diluent gas such as nitrogen, hydrogen, or a C₁-C₅ hydrocarbon. In the case of metal reduction, the desorption inlet gas may be hydrogen. Such desorption inlet gases may be added to the process as a make-up stream through line **121**.

Instead of or in addition to the make-up stream in line **121**, some or all of the adsorption effluent stream flowing in line **114** can be used as desorption gas. To use the adsorption effluent stream as the desorption inlet gas, valve **119** is opened so that the adsorption effluent stream flows through line **118**, valve **119**, and line **120**. If one portion of the

adsorption effluent stream in line 114 flows through line 116 and another portion flows through line 118, then preferably each portion is an aliquot portion of the adsorption effluent stream flowing in line 114. To induce at least some of the adsorption effluent stream to flow through the desorption bed 138, a compressor (not shown) is in or downstream of line 118 while being in or upstream of line 156 and preferably upstream of exchanger 123. The stream flowing in line 122 is thus formed from the make-up stream (if any) flowing in line 121, the adsorption effluent stream flowing in line 120, or both streams.

The stream flowing in line 122 is heated by indirect heat transfer in exchanger 123, flows through line 124, and is further heated to the desired inlet temperature for desorption in heater 126. After heating, the gases flow through line 127 and combine with a make-up stream (if any) in line 128. The make-up stream can be used to add water (or a compound that forms water) to the gases in order to help halogen desorption. The gases flowing in line 130 flows through valve 132, line 134, and line 136, and enter bed 138, which contains adsorbent containing halogen-containing materials. Bed 138 operates in desorption mode, and halogen-containing materials on the adsorbent are desorbed and exit with the effluent of desorption bed 138. When desired, a portion of the gases flowing through line 134 may be made to bypass desorption bed 138 through lines 142 and 146, provided that bypass valve 144 is open.

Desorption bed 138 effluent flows through line 140, combines with any bypass flow in line 146, and flows through line 148, valve 150, and line 152. The stream flowing in line 152 may be cooled using exchanger 154, if needed to achieve the desired inlet temperature for off-stream reactor 64. After any cooling, the desorption effluent stream flows through line 156 and combines with the stream flowing in line 88.

The operating conditions for the process of this invention are determined by many factors, but a primary factor is the regeneration conditions of the off-stream reactor. The regeneration conditions for the off-stream reactor 64 usually include an inlet temperature, an inlet gas hourly space velocity, an inlet oxygen concentration, and an inlet molar ratio of water to halogen of the combustion gases flowing in line 63, a peak or maximum temperature of the catalyst bed in off-stream reactor 64, and an outlet temperature of the flue gases flowing in line 66. In practice, when the halogen is chlorine the molar ratio of water to halogen is the molar ratio of water to chloride. Of course, the specific target values of each of these regeneration variables depends on the composition and nature of the catalyst being regenerated, on the process and mechanical details of the off-stream reactor 64 and other associated equipment (such as exchangers 82 and 123 and compressor 78), and on the regeneration step that is actually taking place. A person of ordinary skill in the art is able to determine the values of these regeneration variables.

The desired inlet conditions of off-stream reactor 64 may or may not be the same, or substantially the same, as the outlet conditions of desorption bed 138. Since the flow rate of the gas stream flowing in line 156 is a relatively small fraction of the flow rate of the gas stream flowing in line 88, changes in the composition and outlet conditions of the stream flowing in line 140 have a relatively small effect on the inlet conditions of off-stream reactor 64. Nevertheless, the desorption outlet conditions may be such that the gas flowing in line 140, when combined with the gas stream flowing in line 88, provides the desired inlet conditions for off-stream reactor 64. In that case, the bypass valve 144 would be closed, and there would be neither heat exchange

by heat exchanger 154, nor halogen addition through line 92, nor water addition through line 96. To achieve those, or any of the possible outlet conditions for the desorption bed 138 without undue experimentation, a person of ordinary skill in the art can monitor the desorption conditions and adjust the inlet conditions of the desorption bed 138 as necessary. The inlet temperature is set by the heater 126. Generally, the desorption temperature is higher than the adsorption temperature and above about 66° C. (150° F.). The desorption temperature is usually from about 260° C. (500° F.) to about 538° C. (1000° F.). The inlet gas hourly space velocity is set by the controlling the flow rates of the adsorption effluent through line 120 and of the make-up stream in line 121. The inlet oxygen concentration to desorption bed 138 is set by the make-up air addition (if any) via line 121. The inlet molar ratio of water to halogen is preferably extremely high (i.e., little or no halogen in the inlet gas, since any halogen in the inlet gas to desorption bed 138 would deter desorption. Such low halogen concentrations are achieved by adsorption in adsorption bed 108.

With bed 138 in desorption mode, the outlet conditions of desorption bed 138 will change over time. This might happen because the adsorbent in desorption bed 138 has become depleted of halogen, resulting in a gradual and ultimately unacceptable increase in the molar ratio of water to halogen in the desorption outlet gas. When this occurs, the positions of bed 138 and bed 108 may be switched, so that bed 138 is used for adsorption, and adsorption bed 108 is used for desorption.

The duration of time that a bed of adsorbent is in desorption mode and the frequency at which the bed is switched from desorption mode depends on many factors. These factors include the desorption conditions, the type and amount of adsorbent, the type of halogen-containing materials, the residual or minimum capacity of the adsorbent for halogen at desorption conditions, the halogen content of the adsorbent, the molar ratio of water to halogen in the stream entering the bed of adsorbent, and the halogen concentration in the effluent of the bed of adsorbent. The halogen content in the desorption effluent is usually at least 1 wt-%, and more commonly at least 10 wt-%, greater than the halogen concentration in the desorption inlet. If less halogen is desorbed from a bed of adsorbent, the bed is removed from desorption mode and replaced with another bed.

It may be desirable to extend the time that a bed of adsorbent is in desorption mode while still maintaining the outlet conditions of the desorption bed the same, or substantially the same. One possible way of simultaneously achieving these two objectives is to add water (or a compound that forms water after being added, such as an alcohol) to the gases that enter the desorption bed 138. Water in the inlet gases to desorption bed 138 helps desorb halogen from the adsorbent, and this is beneficial when the halogen content of the desorption outlet gases declines as the desorption bed 138 becomes depleted of halogen. Although the point of water introduction to the process could be anywhere downstream of line 118 and upstream of desorption bed 138, it is preferred to add water at a point where the process temperature is relatively high, such as through line 128 downstream of heater 130.

Another way of not only extending the time that a bed of adsorbent is in desorption mode but also maintaining substantially constant outlet conditions of the desorption bed is to use two beds containing adsorbent in a parallel flow arrangement for desorption. Initially, only one bed of adsorbent is being desorbed, and all of the desorption gases flow

to that one bed. However, as that desorption bed becomes depleted of halogen, the halogen content in that bed's effluent declines. When the composition of the desorption effluent is no longer the same, or substantially the same, as the desired composition of the regeneration inlet, a second bed of adsorbent is placed in a parallel flow arrangement with the first bed, and some of the desorption gases are routed to the second bed. While both beds are being desorbed, the flow rate of the desorption gases to the two beds is split so that a greater portion of the desorption gases flows to the first, more-depleted bed and a smaller portion of the desorption gases flows to the second, less depleted bed. In this way, the increase in halogen contributed by desorption of the second bed makes up for the decline in halogen contribution from the first bed, so that the total amount of halogen to the off-stream reactor is constant. Accordingly, the first bed of adsorbent may remain in desorption mode for a longer period of time than it could have remained if it alone was used to achieve the desired inlet conditions of the off-stream reactor. When the first bed is sufficiently depleted of halogen, the second desorption bed functions as the first desorption bed, and a third desorption bed replaces and functions as the second desorption bed.

The adsorption conditions are generally selected in order to recover a target or desired fraction of the total amount of the halogen that flows in line 98. In the embodiment shown in the drawing, that total amount of halogen is equal to the amount of halogen that enters the adsorption bed 108 in line 106, and the amount of halogen that is lost (i.e., not recovered) is the amount of halogen in the gas stream that exits the adsorption bed 108 and then exits the process in line 116. Since the flow rates and halogen concentrations of the streams entering and leaving the adsorption bed 108 may vary with time, halogen recovery is determined by time-averaging the amount of halogen entering and exiting the adsorption bed 108. Thus, the amount of halogen entering the adsorption bed 108 can be computed by measuring the flow rates and halogen concentrations of the inlet stream at specified times, plotting a curve representing the product of each flow-rate-concentration data pair versus time, and then integrating the area under the curve. The amount of halogen leaving the adsorption bed 108 can be computed in a similar way, and the halogen recovery is the quotient of the amount leaving divided by the amount entering, expressed as a percentage and subtracted from 100%. Halogen recovery is generally greater than about 80 wt-% and preferably greater than 90 wt-%.

The halogen recovery is determined by many factors. The molar ratio of water to halogen of the inlet gas to the adsorption bed 108 certainly affects the recovery, but this operating variable is not one that a person of ordinary skill in the art practicing this invention would typically control. This is because this ratio is essentially the same as that of the flue gas exiting the off-stream reactor 64, which in turn is determined in large part by the previously-mentioned inlet conditions to off-stream reactor 64 and by the regeneration reactions that take place in the off-stream reactor 64. Generally, as the molar ratio of water to halogen increases, halogen recovery decreases. The molar ratio of water to hydrogen halide in the stream entering the adsorbent bed being used for adsorption is usually more than about 5:1, and depending on the catalyst being regenerated in the reactor as well as other factors, this molar ratio could conceivably be as high as about 50:1 or 100:1.

A second factor affecting halogen recovery is the halogen content of the adsorbent at the start of the adsorption step. Generally, as the initial halogen content increases, the halo-

gen recovery decreases. This initial halogen content is the same as the final halogen content of the adsorbent used for desorption, since the bed of adsorbent that is used for adsorption had previously been used for desorption. For this reason, the extent to which halogen is desorbed during the desorption step can influence the halogen recovery in the adsorption step. But, for the same reason, this variable cannot be independently controlled once the desorption step is finished and the adsorption step begins.

A third variable that can be independently adjusted to affect halogen recovery during adsorption is the adsorption temperature. Adsorption temperature can be controlled by regulating exchangers 123 and 100. Generally, recovery increases as adsorption temperature decreases. Thus, if during adsorption, the halogen recovery drops below the desired target, the adsorption temperature may be decreased to the low end of the range of adsorption temperatures.

The operating temperature for adsorption mode is generally lower than that for desorption mode. The adsorption temperature is usually above about 66° C. (1500° F.). The adsorption temperature is usually no higher than the outlet temperature of the reactor that is undergoing regeneration, but usually it is lower than that by at least 55° C. (100° F.) due to heat exchange between the outlet of the off-stream reactor 64 and the inlet of the desorption bed 108. Only rarely would the adsorption temperature exceed 482° C. (900° F.). The adsorption temperature is generally maintained above the dew point temperature of the flue gas in order to minimize the possibility of condensing corrosive acidic liquid in the adsorption equipment. Also, the adsorption temperature is preferably maintained above the capillary condensation temperature of the flue gas, which is the temperature at which condensation from the flue gas occurs in the capillaries of the adsorbent. The capillary condensation temperature is usually higher than the dew point temperature of the bulk flue gas.

The capillary condensation temperature depends on many factors, including not only the composition of the flue gas but also the chemical and physical properties of the adsorbent, such as the distribution of pore size and volume. When there are differences in the physical dimensions and chemical components of individual pores of the adsorbent, capillary condensation will occur over a range of temperatures. The greater the amount of capillary condensation during adsorption, the greater is the amount of water present on the adsorbent at the start of the desorbent step. To the extent that this greater amount of water is desorbed during the desorption step, the greater is the amount of water withdrawn from the reactor undergoing regeneration and returned or recycled to the reactor.

The capillary condensation temperature can be approximately determined from a graph of the weight of water adsorbed on the adsorbent as a function of adsorption temperature of the flue gas. As temperature is decreased from above the range of capillary condensation temperatures into the range of temperatures where capillary condensation occurs, the slope of the graph increases dramatically. While the change in slope may occur over a range of temperatures rather than at one particular temperature, the change is nevertheless apparent to a person of ordinary skill in the art. For example, if the upper end of the range of capillary condensation temperature is 149° C. (300° F.), the change in the weight of water adsorbed may be only about 1.5 wt-% as the temperature is decreased from about 427° C. (800° F.) to about 149° C. (300° F.), but may be about 4 wt-% as the temperature is further decreased from about 149° C. (300° F.) to about 121° C. (250° F.). In addition, a person of

ordinary skill in the art can estimate the capillary condensation temperature by estimating the difference between the dew point temperature of the bulk flue gas and the capillary condensation temperature using well-known correlations and theoretical techniques that take into account the dimensions of the adsorbent's capillaries and other factors, and then adding that difference to the measured dew point temperature.

Despite decreasing the adsorption temperature to increase halogen recovery, halogen recovery may nevertheless be unacceptably low, because of frequent or excessive breakthrough of halogen into the outlet of the adsorption bed **108**. In this case, other embodiments of this invention can be used to further improve halogen recovery. Instead of, or subsequent to, operating the desorption bed **138** so that the outlet conditions of desorption bed **138** are maintained the same as, or substantially the same, the desorption operating variables may be selected more independently of the regeneration conditions. In these other embodiments of this invention, desorption operating conditions are selected with the objective of decreasing the final halogen content of the adsorbent at the end of the desorption step. This objective can be met in several ways. First, the desorption temperature can be increased to a temperature above the desired regeneration inlet temperature. Heater **126** can heat the gases entering desorption bed **138**, and exchanger **154** can cool the exiting gases to the desired temperature for combining with the gases flowing through line **88** and achieving a desired inlet temperature of off-stream reactor **64**. Second, the desorption step can be prolonged beyond the point when the outlet molar ratio of water to halogen increases above that desired, taking into consideration the molar ratio in the stream flowing in line **88**. In that case, line **92** may be used to add halogen to the gases flowing in line **94**, thereby lowering the molar ratio to the desired range for the inlet of the off-stream reactor **64**.

Even if halogen recovery is within the desired range, the outlet conditions of the desorption bed **138** may not be what is desired for mixing the stream flowing in line **156** with the stream flowing in line **88** to achieve the desired inlet conditions of the off-stream reactor **64**. For example, the molar ratio of water to halogen in the gases flowing through line **140** may be lower than desired to attain a given molar ratio at the inlet of the off-stream reactor **64**. This can happen if too much halogen is being desorbed too rapidly from the desorption bed **138**, such as when desorption is starting on a bed of adsorbent that adsorbed an excessive amount of halogen or when the gas is flowing through the bed at an excessive rate. In these situations, a surge of halogen may be desorbed from the bed, resulting in an unacceptably low molar ratio of water to halogen in the gases flowing through line **140**. In these circumstances, either or both of two other embodiments of this invention are useful. First, line **96** may be used to add water to the gases flowing through line **94**, thereby raising the molar ratio to the desired range for the inlet of off-stream reactor **64**. Second, valve **144** may be opened to bypass desorption gases around desorption bed **138**, thereby decreasing the amount of halogen that is desorbed from the adsorbent in desorption bed **138** and effectively raising the molar ratio of the gases flowing through line **60** to the desired range. In either event, once the molar ratio of water to halogen in the gases flowing through line **140** increases to the desired range, the water addition or the desorption gas bypassing may be decreased or stopped.

When halogen breakthrough occurs in the effluent of the bed of adsorbent that is being used for adsorption, the bed is removed from adsorption mode, and is subsequently used

for desorption. The duration of time that the bed is in adsorption mode and the frequency at which the bed is removed from adsorption mode depends on many factors. These factors include the adsorption conditions, the type and amount of adsorbent, the type of halogen-containing materials, the maximum capacity of the adsorbent for halogen at adsorption conditions, the halogen content of the adsorbent, the molar ratio of water to halogen in the stream entering the bed of adsorbent, and the halogen concentration in the adsorbent bed. A bed of adsorbent used in adsorption mode adsorbs usually at least 90 wt-%, and preferably at least 99 wt-%, of the halogen in the stream entering the bed of adsorbent. If less halogen than that is adsorbed by the bed of adsorbent, the bed is removed from adsorption mode and replaced with another bed.

Although the description of this invention has been mainly in terms of two beds of adsorbent, one in use for adsorption and the other in use for desorption, there may of course be more beds of adsorbent, and at any given time some of these other beds might be in use for adsorption, desorption, or neither. One or more beds of adsorbent may have already been used for adsorption and are awaiting desorption, while others have been used for desorption and are awaiting adsorption. Such additional adsorbent beds may be desirable for several reasons. First, one or more additional beds may be useful if there is a heating step between the adsorption and desorption steps, to preheat the relatively cool adsorbent after adsorption and prior to desorption. Also, additional beds may be used if there is a cooling step after desorption and prior to adsorption. Third, additional beds may be used if the adsorbent beds have a relatively small capacity for halogen relative to the amount of halogen that may be removed from the off-stream reactor bed **64** and vented through line **98**. Fourth, additional beds could function as a "reservoir" for halogen that had been removed from the off-stream reactor but which had not yet been returned to the reactor. Such a situation may arise when the regeneration conditions do not require that halogen removed from the catalyst be returned immediately to the off-stream reactor.

A fifth reason that additional beds may be desirable is that the additional beds may be used to maximize halogen recovery. In one example, a bed that is being used for adsorption could be replaced with a fresh bed either long before any halogen breaks through at the outlet of the bed or well prior to when the halogen content of the adsorbent in the bed in adsorption mode has reached its maximum content. By not operating the adsorption bed to the point of maximum possible halogen loading, the full halogen capacity of the adsorbent may not be utilized, but since the risk of halogen breakthrough is minimized, halogen recovery is maximized. In another example, two beds containing adsorbent could be used in a series flow arrangement for a "lead-lag" adsorption operation. The first bed in the series, or the "lead" bed, could be used for adsorption up to or even after either halogen breaks through at the outlet of the "lead" bed, or the halogen content of the adsorbent in the "lead" bed has reached its maximum. The second bed in the series, or the "lag" bed, could adsorb any halogen that breaks through the "lead" bed. By operating the "lead" bed to the point of its maximum possible halogen loading, the full halogen capacity of the adsorbent in the "lead" bed is utilized while still maximizing halogen recovery. When halogen breakthrough has occurred in the outlet of the "lead" bed, the "lead" bed is removed from adsorption mode and replaced with the "lag" bed, and the "lag" bed is replaced with a bed that has been used for desorption.

As previously described, halogen recovery is affected by the difference between the halogen content of the adsorbent

prior to adsorption (i.e., after desorption) and the halogen content of the adsorbent after adsorption (i.e., prior to desorption). Generally, the greater the difference in halogen contents, the greater is the halogen recovery. Suitable halogen recoveries are achieved when the difference between the halogen content of the adsorbent prior to adsorption (i.e., after desorption) and the halogen content of the adsorbent after adsorption (i.e., prior to desorption) is from about 0.2 to about 2.0 wt-% halogen, and preferably from about 0.5 to about 1.0 wt-% halogen, based on the weight of the adsorbent.

The difference in halogen contents of the adsorbent depends on many factors, including the flow rates and compositions of the gases flowing through the adsorption and desorption beds, the adsorbent, the quantities of adsorbent used for adsorption and desorption, and other adsorption and desorption conditions, especially the difference between the adsorption and desorption temperatures. As long as there is some difference in the adsorption and desorption temperatures, then some adsorption of halogen will generally occur. With all other conditions being the same, the greater the difference in adsorption and desorption temperatures, the greater is the recovery of halogen. This increased recovery is due to either an increase in halogen pickup during adsorption (due to a lower adsorption temperature) or an increase in halogen removal during desorption (due to a higher desorption temperature). The difference in the adsorption and desorption temperatures is usually more than about 55° C. (100° F.). The difference in halogen contents also depends on the molar ratios of water to halogen during adsorption and desorption. The ratio of the molar ratio of water to halogen during adsorption to the molar ratio of water to halogen during desorption is generally from about 0 to about 2.

The relationship between, on the one hand, halogen recovery and, on the other hand, the flow rates and halogen concentrations of the streams during adsorption and desorption and the amount of adsorbent used for adsorption and desorption is that of a halogen material balance. Thus, assuming that the adsorbent in the adsorption bed has adequate capacity to adsorb a desired amount of halogen, it is possible to adsorb that amount either by using a relatively high flow rate of the gas at a relatively low inlet concentration of halogen or by using a relatively low flow rate of the gas at a relatively high concentration of halogen. Similarly, a desired amount of halogen can be desorbed from the desorption bed with either a relatively high or low flow rate of gas or with a relatively low or high concentration of halogen.

As used herein, the term "halogen" includes "halogen" or "halide." Thus, the term "halogen" includes an IUPAC Group 17 (VII B) element component such as fluorine, fluoride, chlorine, chloride, bromine, bromide, iodine, iodide, etc. The term "halogen-containing material" includes molecules or compounds containing halogen, regardless whether they are present on the catalyst, on the adsorbent, or in a fluid stream. But, in the case of molecules or compounds present on the catalyst or the adsorbent, the term "halogen-containing material" means the halogen or halide itself, rather than the catalyst or the adsorbent. That is, even when a catalyst or an adsorbent contains halogen, referring to the "halogen-containing material" on the catalyst or adsorbent does not refer to the catalyst or the adsorbent itself as a whole, but rather to the halogen or halide present on the catalyst or adsorbent.

All references herein to groups of elements are to the Periodic Table of the Elements, "CRC Handbook of Chemistry and Physics," CRC Press, 80th Edition, 1999–2000.

We claim:

1. A process for the regeneration of a hydrocarbon conversion catalyst in the presence of a halogen-containing material, the process comprising:

- (a) contacting a regeneration inlet stream comprising a first component selected from the group consisting of oxygen, hydrogen, nitrogen, and a C₁–C₅ hydrocarbon with a catalyst in the presence of a halogen-containing material at regeneration conditions to at least partially regenerate said catalyst and produce a regeneration effluent stream comprising said material and said first component;
- (b) contacting a first portion of said regeneration effluent stream with an adsorbent, adsorbing said material on said adsorbent at adsorption conditions, and recovering an adsorption effluent stream comprising said first component and having a reduced concentration of said material relative to said first portion of said regeneration effluent stream;
- (c) contacting a desorption inlet stream comprising a second component selected from the group consisting of oxygen, hydrogen, nitrogen, and a C₁–C₅ hydrocarbon with said adsorbent, said adsorbent having said material adsorbed thereon, desorbing said material from said adsorbent at desorption conditions, and recovering a desorption effluent stream comprising said material and said second component; and,
- (d) forming said regeneration inlet stream from a second portion of said regeneration effluent stream and at least a portion of said desorption effluent stream.

2. The process of claim 1 wherein said adsorbent is selected from the group consisting of a molecular sieve, silica gel, carbon, and alumina.

3. The process of claim 1 wherein said catalyst is selected from the group consisting of a reforming catalyst, an isomerization catalyst, and a dehydrogenation catalyst.

4. The process of claim 1 wherein said regeneration is selected from the group consisting of burning carbon deposits on said catalyst, redispersing a metal on said catalyst, adding halogen to said catalyst, drying said catalyst, and reducing a metal on said catalyst.

5. The process of claim 1 further characterized in that at least about 80 percent of said material in said regeneration effluent stream is adsorbed on said adsorbent.

6. The process of claim 1 further characterized in that at least about 90 percent of said material in said regeneration effluent stream is adsorbed on said adsorbent.

7. The process of claim 1 further characterized in that said adsorption conditions comprise a temperature of less than about 482° C. and a molar ratio of water to halogen of more than 5:1.

8. The process of claim 1 further characterized in that said adsorbent has a capillary condensation temperature at said adsorption conditions, and said adsorption conditions comprise a temperature of greater than said capillary condensation temperature.

9. The process of claim 1 wherein said halogen is chlorine or fluorine.

10. The process of claim 1 wherein said material is selected from the group consisting of hydrogen chloride and molecular chlorine.

11. The process of claim 1 further characterized in that said adsorbent has a pre-adsorption halogen content prior to said contacting and said adsorbing in (b), said adsorbent has a post-adsorption halogen content after said contacting and said desorbing in (c), and the difference between said pre-adsorption halogen content and said post-adsorption

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halogen content is from about 0.2 to about 2.0 wt- % halogen, based on the weight of the adsorbent.

12. The process of claim 1 further characterized in that said regeneration inlet stream has a regeneration inlet temperature and a regeneration inlet molar ratio of water to halogen, said desorption effluent stream has a desorption effluent temperature and a desorption effluent molar ratio of water to halogen, the difference between said regeneration inlet temperature and said desorption effluent temperature is less than about 20° C., and the difference between said regeneration inlet molar ratio and said desorption effluent molar ratio is less than about 5:1.

13. The process of claim 1 further characterized in that the adsorption conditions comprise an adsorption temperature and an adsorption molar ratio of water to halogen, the desorption conditions comprise a desorption temperature and a desorption molar ratio of water to halogen, the difference between the desorption temperature and the adsorption temperature is more than about 55° C., and the ratio of the adsorption molar ratio to the desorption molar ratio is from about 0 to about 2.

14. The process of claim 1 further characterized in that a component consisting of at least one of water and a compound that can react to form water is introduced into said process and said water contacts said adsorbent in (c).

15. The process of claim 1 further characterized in that at least one of said second portion of said regeneration effluent stream, said at least a portion of the desorption effluent stream, and the regeneration inlet stream is cooled.

16. A sorptive method for recovering a chlorine-containing material from the outlet stream of a cyclic regeneration operation of a hydrocarbon conversion process using a hydrocarbon conversion catalyst, said method comprising:

- (a) passing hydrocarbons to a first catalyst bed containing a hydrocarbon conversion catalyst and converting said hydrocarbons;
- (b) passing a regeneration inlet stream comprising a first component selected from the group consisting of oxygen, hydrogen, nitrogen, and a C₁-C₅ hydrocarbon to a second catalyst bed containing said hydrocarbon conversion catalyst, at least partially regenerating said hydrocarbon conversion catalyst in said second catalyst bed at regeneration conditions and in the presence of a chlorine-containing material, and recovering from the second catalyst bed a regeneration effluent stream comprising said material and said first component;
- (c) passing a first portion of said regeneration effluent stream to an adsorption zone containing an adsorbent,

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adsorbing said material on said adsorbent at adsorption conditions, and recovering an adsorption effluent stream comprising said first component and having a reduced concentration of said material relative to said regeneration effluent stream;

- (d) passing a desorption inlet stream comprising a second component selected from the group consisting of oxygen, hydrogen, nitrogen, and a C₁-C₅ hydrocarbon to a desorption zone containing said adsorbent, said adsorbent in said desorption zone having said material adsorbed thereon, desorbing said material from said adsorbent in said desorption zone, and recovering a desorption effluent stream comprising said material and said second component;
- (e) forming said regeneration inlet stream from a second portion of said regeneration effluent stream and at least a portion of said desorption effluent stream; and
- (f) at least periodically shifting the functions of said adsorption and desorption zones by operating said adsorption zone to function as said desorption zone in (d), and operating said desorption zone to function as said adsorption zone in (c).

17. The process of claim 16 further characterized in that the functions of said first and second catalyst beds are at least periodically shifted by operating said first catalyst bed to function as said second catalyst bed in (b), and operating said second catalyst to function as said first catalyst bed in (a).

18. The process of claim 16 wherein said hydrocarbon conversion process is a process selected from the group consisting of reforming, isomerization, and dehydrogenation.

19. The process of claim 16 wherein said regeneration is selected from the group consisting of burning carbon deposits on said catalyst, redispersing a metal on said catalyst, adding halogen to said catalyst, drying said catalyst, and reducing a metal on said catalyst.

20. The process of claim 16 further characterized in that at least about 80 percent of said material in said regeneration effluent stream is adsorbed on said adsorbent.

21. The process of claim 16 further characterized in that said desorption inlet stream is formed at least a portion of said adsorption effluent stream.

22. The process of claim 21 wherein said first component is said second component.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,790,802 B1
DATED : September 14, 2004
INVENTOR(S) : Paul A. Sechrist

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 16,
Line 45, immediately following "formed," insert -- from --.

Signed and Sealed this

Seventh Day of December, 2004

A handwritten signature in black ink on a light gray dotted background. The signature reads "Jon W. Dudas" in a cursive style.

JON W. DUDAS

Director of the United States Patent and Trademark Office